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PATENT ABSTRACTS OF JAPAN

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(71)Applicant : **SONY CORP**

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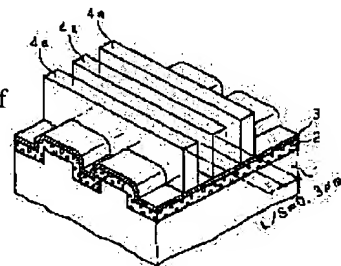
(72)Inventor : **TO YOICHI**

(54) ANTIREFLECTION FILM AND PATTERN FORMING METHOD USING THIS FILM

(57)Abstract:

PURPOSE: To form a pattern at a high dimensional accuracy, using an conformal organic pigment type antireflection film.

CONSTITUTION: An antireflection film 3 uses a conformal vapor deposition film made of a nonmetallic phthalocyanine which is solvable with a solvent having a higher polarity than that of a photoresist solvent and absorbs a light in a wavelength range of 140-450nm. A photoresist pattern 4a is formed on this film by the exposure and development, the surface of the film 3 is removed by an O₂-plasma RIE and base material film 2 is anisotropically etched. The pattern 4a and antireflection film pattern are removed at once by applying an inorganic or organic resist peeling liq. or ashing.. In an excimer laser lithography, the antireflection effect is equalized in a substrate plane whereby the dimensional variation of the pattern 4a can be suppressed.



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CLAIMS

[Claim(s)]

[Claim 1] The antireflection film which consists of an organic compound in which it is more nearly meltable than a photoresist solvent to the solvent which has high polarity, and an optical absorption is shown in a 150-450nm wavelength region.

[Claim 2] The above-mentioned organic compound is an antireflection film according to claim 1 which is a non-metal alkoxy substitution phthalocyanine.

[Claim 3] The above-mentioned organic compound is an antireflection film according to claim 1 which is a non-metal-alkyl substitution phthalocyanine.

[Claim 4] The above-mentioned organic compound is an antireflection film according to claim 1 which is a non-metal halogenation phthalocyanine.

[Claim 5] The above-mentioned organic compound is an antireflection film according to claim 1 which is non-metal a non-replaced phthalocyanine.

[Claim 6] The pattern-formation method of having the process which forms an antireflection film given in any 1 term of a claim 1 or a claim 3 by the vapor growth on a furring film, the process which forms a photoresist pattern on the aforementioned antireflection film, the process which *****s the aforementioned antireflection film and the aforementioned furring film in different direction one by one by using the aforementioned photoresist pattern as a mask, and the process which removes the aforementioned photoresist pattern and the aforementioned antireflection film using organic system resist ablation liquid.

[Claim 7] The pattern formation method of having the process which forms an antireflection film given in any 1 term of a claim 1 or a claim 4 by the vapor growth on a furring film, the process which forms a photoresist pattern on the aforementioned antireflection film, the process which *****s the aforementioned antireflection film and the aforementioned furring film in different direction by using the aforementioned photoresist pattern as a mask, and the process which removes the aforementioned photoresist pattern and the aforementioned antireflection film using inorganic system resist ablation liquid.

[Claim 8] The pattern formation method of having the process which makes any 1 term of a claim 1 or a claim 5 carrying out the vapor growth of the antireflection film of a publication on a furring film, the process which forms a photoresist pattern on the aforementioned antireflection film, the process which *****s the aforementioned antireflection film and the aforementioned furring film in different direction by using the aforementioned photoresist pattern as a mask, and the process which performs ashing and removes the aforementioned photoresist pattern and the aforementioned antireflection film.

[Claim 9] The aforementioned vapor growth is the pattern formation method given in any 1 term of the claim 6 which is a vacuum deposition method, or a claim 8.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the antireflection film which consists of an organic compound in which especially conformal membrane formation is possible, and the pattern formation method which can perform line breadth control with high precision using this about the pattern formation method using the antireflection film and this which are applied to micro processing, such as semiconductor-device manufacture.

[0002]

[Description of the Prior Art] High integration of a semiconductor device follows on going on at an increasing tempo, and the minimum processing size is also reduced quickly. For example, although the minimum processing size of 16MDRAMs of current generation which has shifted to the mass-production line is about 0.5 micrometers, at 64MDRAMs of the next generation, 0.35 micrometers or less are expected to be reduced to 0.25 micrometers or less by a generation's 256MDRAMs one after another.

[0003] It depends for this degree of detailed-izing on the resolution of the photolithography process which forms a mask pattern greatly. In processing of 0.35 micrometers - 0.25 micrometer (deep submicron) class, the far-ultraviolet light sources, such as KrF excimer laser light (wavelength of 248nm), are needed. However, in the process using such the homogeneous light, since the fall of the contrast by halation or the standing wave effect or resolution appears notably, it is thought that it becomes indispensable to use an antireflection film in order to weaken the reflected light from a furring film.

[0004] It divides roughly into an antireflection film, and is connected with the character of the membrane formation method or a film, and there are a spin coat type and a conformal membrane formation type. Among these, the antireflection film which can be cheaply used with the comparatively few number of processes is the former spin coat type.

[0005] A spin coat type antireflection film makes a subject the organic polymer containing the color which has optical absorption sufficient in an exposure wavelength region, is applied on a furring film using a spin coater, and is formed through baking. Patterning of a photoresist is performed on this. It is [the type (for example, SWK/ by TOKYO OHKA KOGYO CO., LTD. /- 436) by which is meltable to a spin coat type antireflection film, and patterning is simultaneously carried out to a resist developer at it at the time of development, and] O2 after resist development. There is a type (for example, DUV[by BURYUWA Saiensu-Sha Co., Ltd.]- 11) by which is removed by Plasma RIE and pattern formation is carried out. Any type can ease the reflection from a furring film by the optical-absorption ability.

[0006]

[Problem(s) to be Solved by the Invention] However, since it is easy to produce the thickness change resulting from the level difference of a furring film since membranes are formed by the spin coater, and the acid-resisting effect varies on a substrate, an above-mentioned spin coat type antireflection film has the problem of being easy to cause line breadth change of a photoresist pattern as a result. Especially, in a thing meltable to a resist developer type, compared with a membranous thick portion, the dissolution progresses quickly in a thin portion, and there is an inclination for line breadth to become thin.

[0007] Therefore, in order to attain the dimensional stability which was excellent using the spin coat type antireflection film, it is required to fully carry out flattening of the substrate front face. However, in a semiconductor device in recent years, it is in the inclination to originate in adoption of a multilayer interconnection and for the surface level difference of a substrate to increase, and flattening is not always easy in all the stages of a semiconductor process so that memory devices, such as DRAM and SRAM, may see.

[0008] On the other hand, although the problem of thickness change will be fundamentally solved if it is a conformal membrane formation type antireflection film, this type of conventional antireflection film has many which formed the inorganic compound by technique, such as CVD and PVD, and there are few things using the organic compound. However, when expanding the selection width of face of a process using the versatility of a compound, the meaning which develops the conformal membrane formation type antireflection film which consists of an organic compound is large.

[0009] Then, this invention aims at offering the high pattern formation method of a dimensional accuracy using the antireflection film which consists of an organic compound in which conformal membrane formation is possible, and this.

[0010]

[Means for Solving the Problem] this invention is more nearly meltable than a photoresist solvent to the solvent which has high polarity, and the above-mentioned purpose is attained with the antireflection film which consists of an organic compound

in which an optical absorption is shown in a 150-450nm wavelength region.

[0011] Here, as an example of representation of the solvent generally used as the above-mentioned photoresist solvent, ethylcellosolve acetate (ECA), an ethyl lactate (EL), pyruvic-acid ethyl (EP), butyl acetate (bus available), propylene-glycol-monomethyl-ether acetate (PMA), ethyl-3-ethoxy propionate (EEP), or these mixed solvents exist.

[0012] Therefore, as a solvent which has polarity higher than this, a tetrahydrofuran (THF), ethyl acetate, an acetone, ethanol, a methanol, and water can be illustrated. Since the organic compound which constitutes the antireflection film of this invention is meltable only to these high polar solvents, it is not eluted at all at the process which applies photoresist material.

[0013] Excimer laser light, such as a bright line spectrum of high-pressure mercury lamps, such as g line (436nm) and i line (365nm), and XeCl (308nm), and KrF (248nm), ArF (193nm), is contained in the above-mentioned wavelength region.

[0014] Moreover, as the above-mentioned organic compound, it can use in any of a non-metal alkoxy substitution phthalocyanine, a non-metal-alkyl substitution phthalocyanine, a non-metal halogenation phthalocyanine, and a non-metal a non-replaced phthalocyanine. In addition, thereby in these phthalocyanine system compounds, optical-absorption ability [in / specific exposure wavelength / it is possible to carry out the molecular design of the compound in which various optical-absorption spectrums are shown based on the kind and combination of a substituent, and] can be changed variously.

[0015] this invention attains the above-mentioned purpose with the pattern formation method of having the process which removes the process which forms either of the above-mentioned antireflection films on a furring film by the vapor growth, the process which forms a photoresist pattern on this antireflection film, the process which *****s the aforementioned antireflection film and the aforementioned furring film in different direction one by one by using this photoresist pattern as a mask, and the aforementioned photoresist pattern and the aforementioned antireflection film again.

[0016] Here, RIE (reactive ion etching) can perform typically different direction-etching of the above-mentioned antireflection film and the above-mentioned furring film one by one using the conditions optimized for [each] films. Since especially the above-mentioned antireflection film is a film which consists of an organic compound, if oxygen system plasma is used, it is easily removable.

[0017] Furthermore, at the process which removes the aforementioned photoresist pattern which ended a role of an etching mask, and the aforementioned antireflection film, the removal methods differ by using which phthalocyanine system compound the above-mentioned antireflection film is constituted.

[0018] That is, a non-metal alkoxy substitution phthalocyanine and a non-metal-alkyl substitution phthalocyanine are usable to remove a photoresist pattern using organic system resist ablation liquid. As organic system resist ablation liquid in this case, the ablation liquid which makes cresol and a phenol a subject is known.

[0019] Moreover, when using inorganic system resist ablation liquid, in addition to two above-mentioned persons, a non-metal halogenation phthalocyanine can be used. Here, as this phthalocyanine system compound, a non-metal all fluorine substitution phthalocyanine is typical. As inorganic system resist ablation liquid in this case, the strong ablation liquid of oxidizing power, such as a heat concentrated-sulfuric-acid, fuming-nitric-acid, and sulfuric-acid-hydrogen-peroxide mixed solution, can be used.

[0020] Furthermore, since all organic substances will be removed by the combustion reaction when performing ashing, you may use the antireflection film which consists of which phthalocyanine system compound.

[0021] By the way, a vacuum deposition is the most practical although a vacuum deposition method, a plasma polymerization method, and molecular beam epitaxy are mentioned to a candidate as the aforementioned vapor growth adopted as this invention. Although it divides roughly into the heating method of the evaporation source in a vacuum deposition method and there are a resistance heating method and an electron-beam-heating method in it, in the case of the vacuum deposition of an organic compound, the former resistance heating method is used in many cases.

[0022]

[Function] Since the antireflection film of this invention is constituted from a meltable organic compound by the solvent which has polarity higher than a photoresist solvent, it can be used every antireflection film formed ahead of a photoresist paint film, i.e., the so-called bottom, as an antireflection film of type, and can sever the cause of a standing wave and halation from the origin. Moreover, if the non-metal phthalocyanine system compound which has an optical absorption in a 150-450nm wavelength region as this organic compound is used, the good acid-resisting effect can be acquired in g line lithography, an i line lithography, and excimer laser lithography, and resolution can be raised.

[0023] By the vacuum deposition method, since it can deposit on conformal one, the above-mentioned antireflection film can equalize the acid-resisting effect on the whole surface of a substrate. And since the portion expressed from a photoresist pattern among this antireflection film is removed by anisotropic etching, the line breadth change in the formation stage of a photoresist pattern can be suppressed mostly.

[0024] Furthermore, since after the patterning end of a furring film can perform either ablation according the above-mentioned antireflection film to an organic system or inorganic system resist ablation liquid, or ashing according to the kind of used non-metal phthalocyanine system compound and can remove it easily, also as for adjustment with a process, it is conventionally good, and does not have a possibility of leaving contamination on a substrate.

[0025]

[Example] Hereafter, the concrete example of this invention is explained.

[0026] Example 1 this example explains the antireflection film which consists of a non-metal phthalocyanine system compound.

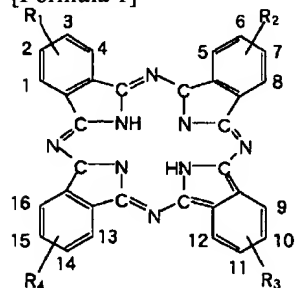
[0027] A part of substrate by which this antireflection film was formed in drawing 1 is shown. The conformal furring film 2 and a conformal antireflection film 3 are formed one by one on the substrate 1 of the diameter of 5 inch which has a level difference resulting from line [of 0.8 micrometer width of face] -, and - space (last shipment), and this drawing shows the state where flattening of the whole surface of a base was further carried out by the photoresist film 4.

[0028] Here, the above-mentioned furring film 2 consists of a polysilicon contest film with a thickness of about 100nm. Moreover, the above-mentioned antireflection film 3 is a phthalocyanine with a thickness of about 50nm or a vacuum deposition film of the derivative. Furthermore, the above-mentioned photoresist film 4 consists of a negative-mold chemistry multiplier system resist (XP8843 made from SHIPURE) whose thickness of a thick portion is about 1 micrometer, for example. Since the above-mentioned antireflection film 3 is insoluble to a resist solvent, on it, also in the process which applies photoresist material, it causes neither the dissolution nor deformation at all, but is maintaining the conformal configuration.

[0029] As the above-mentioned non-metal phthalocyanine system compound, a total of four kinds of compounds, the phthalocyanine shown by next ** 1 (general formula), a tetramethoxy phthalocyanine and a tetrapod-t-butyl phthalocyanine, and the dodeca fluoro phthalocyanine shown in a row by ** 2, were used.

[0030]

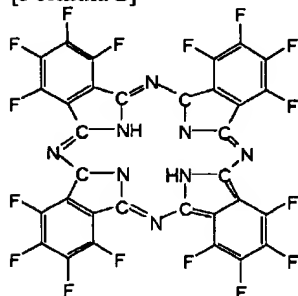
[Formula 1]



(ただし、R₁、R₂、R₃、R₄は各環のβ位のいずれか一方を置換する。)

[0031]

[Formula 2]



[0032] The compound used by this example is substituent R₁ -R₄ shown in ** 1. If it is altogether equal and these are H (hydrogen atom), they are a phthalocyanine and -OCH₃. If it is a machine, it is a tetramethoxy phthalocyanine and -C(CH₃)₃. It is a tetrapod-t-butyl phthalocyanine if it is a machine. However, it sets to ** 1 and is substituent R₁ -R₄. Although the either of the beta grades of each ring, i.e., the 2nd place or the 3rd place, the 6th place, the 7th place, the 10th place, the 11th place and the 14th place, or the 15th place is replaced, this combination does not become settled in one kind. This is substituent R₁ -R₄ of the above [the starting material at the time of composition of a phthalocyanine system compound]. It is the phthalonitrile derivative combined with the 4th place, and is because the combination which reversed the front reverse side of each molecule is possible in case this phthalonitrile derivative tetrad starts a condensation reaction. After fusing the corresponding phthalonitrile derivative above 400 degrees C for several hours and extracting this melt using a Soxhlet extractor and THF, this composition can condense an extract and can be performed by carrying out sublimation refining under reduced pressure of the residue.

[0033] On the other hand, although a dodeca fluoro phthalocyanine cannot perform such direct composition, a commercial phthalocyanine is compoundable by the method of carrying out the fluoridation.

[0034] By example 2 this example, the formation method of a furring film pattern of having used the vacuum deposition film of a tetramethoxy phthalocyanine as the above-mentioned antireflection film 3 is explained, referring to drawing 1 or drawing 5.

[0035] First, the base shown in above-mentioned drawing 1 was prepared. The above-mentioned antireflection film 3 formed membranes by performing resistance heating vacuum evaporation under conditions with a vacuum evaporation temperature

[of 350-400 degrees C], and a degree of vacuum of 0.067Pa.

[0036] The above-mentioned photoresist film 4 formed by performing 110 degrees C and prebaking for 90 minutes, after carrying out the spin coat of the negative-mold chemistry multiplier system resist (XP8843 made from SHIPURE).

[0037] Next, the 0.3-micrometer pattern for line - and - space exposure was projected using the KrF excimer laser stepper (NA=0.42). Then, after performing BEKU after exposure in 140 degrees C and 90 seconds, paddle development for 60 seconds was performed using the developer which diluted the commercial alkali developer (Tokyo adaptation shrine NMD-W), and lowered TMAH (tetramethylammonium hydroxide) concentration to 1.9%, and 110 more degrees C and the postbake for 120 seconds were performed.

[0038] By the above operation, photoresist pattern 4a as shown in drawing 2 was formed. When the line breadth of this photoresist pattern 4a was measured using length measurement SEM (scanning electron microscope), the variation of tolerance during the level difference upper and lower sides is only 0.003 micrometers (1% of a design rule), and it turns out that patterning with a very high precision is performed. This is because the above-mentioned antireflection film 3 conformal membrane formation was carried out [the antireflection film] by the vacuum deposition method demonstrated the uniform acid-resisting effect over the whole surface of a base.

[0039] Next, O₂ RIE using gas was performed, and as shown in drawing 3, the expressional section of an antireflection film 3 was *****ed. Thereby, antireflection film pattern 3a remained in the bottom of photoresist pattern 4a. In addition, since this etching was performed in different direction for a short time, retreat (the so-called film decrease) of photoresist pattern 4a was able to be suppressed to the minimum.

[0040] Next, an owner magnetic field microwave plasma etching system and HBr/O₂ The furring film 2 which consists of a polysilicon contest film using mixed gas was *****ed, and as shown in drawing 4, furring film pattern 2a was formed.

[0041] Next, when ablation processing was performed using RA stripper (fuming nitric acid) which is inorganic system resist ablation liquid, as shown in drawing 5, photoresist pattern 4a and antireflection film pattern 3a were simultaneously removable.

[0042] In example 3 this example, the same pattern formation as an example 2 was performed, using a tetrapod-t-butyl phthalocyanine as a component of an antireflection film 3.

[0043] Here, vacuum deposition of a tetrapod-t-butyl phthalocyanine was performed as an example on conditions with a vacuum evaporatio no temperature [of 250-350 degrees C], and a degree of vacuum of 0.067Pa. Then, when exposure and development were performed like the example 2, the variation of tolerance in the level difference upper and lower sides of formed photoresist pattern 4a was suppressed very small with about 0.003 micrometers. Furthermore, RIE of an antireflection film and a furring film was performed and photoresist pattern 4a was exfoliated using the organic system resist ablation liquid which makes cresol a subject. At this time, the above-mentioned antireflection film pattern 3a was also simultaneously removable.

[0044] In example 4 this example, the same pattern formation as an example 2 was performed, using a dodeca fluoro phthalocyanine as a component of an antireflection film 3.

[0045] Here, vacuum deposition of a dodeca fluoro phthalocyanine was performed as an example on conditions with a vacuum evaporatio no temperature [of 250-300 degrees C], and a degree of vacuum of 0.067Pa. Then, when exposure and development were performed like the example 2, the variation of tolerance in the level difference upper and lower sides of formed photoresist pattern 4a was suppressed very small with about 0.004 micrometers. Furthermore, RIE of an antireflection film 3 and the furring film 2 was performed, ashing was performed, and photoresist pattern 4a and antireflection film pattern 3a were removed simultaneously.

[0046] In addition, although antireflection film pattern 3a of this example which consists of the above-mentioned dodeca fluoro phthalocyanine was removable with the fuming nitric acid besides the above-mentioned ashing, it was not able to remove cresol with the organic system resist ablation liquid made into a subject.

[0047] At the example of the example book comparison of comparison, it is O₂ as comparison to the above example 2 or example 4. The photoresist pattern was formed using the spin coat type antireflection film (DUV[by BURYUWA Saiensu-Sha Co., Ltd.]- 11) of the type removed by Plasma RIE. This process is explained referring to drawing 6 and drawing 7.

[0048] In this example of comparison, after performing formation of the furring film 2 which consists of a polysilicon contest film as mentioned above, it carried out application formation of the spin coat type antireflection film 5 as shown in drawing 6, and carried out flattening of the base front face to after an appropriate time by the photoresist film 4. Here, the above-mentioned spin coat type antireflection film 5 shows a flow configuration, is thin in the level difference upper part, and is thickly formed in the level difference lower part.

[0049] Although photoresist pattern 4b was formed as shown in drawing 7 when KrF excimer laser exposure and the development were similarly performed in this state, the line breadth is 0.295 micrometers in the level difference upper part in 0.32 micrometers and the level difference lower part, and it turns out that the variation of tolerance of the level difference upper and lower sides amounts to no less than 0.025 micrometers (8% or more of a design rule). In addition, in drawing 7, this variation of tolerance is exaggerated and it has expressed. This big variation of tolerance occurred because the quantity of light absorbed by the photoresist film 4 in the level difference upper part increased, the crosslinking reaction of a negative-mold photoresist advanced too much and line breadth was fattened, since the acid-resisting effects in the thin field of an antireflection film 5 ran short relatively.

[0050] As mentioned above, although this invention was explained based on the example of four examples, this invention is not limited to these examples at all.

[0051] For example, the kind and the combination of the removal method of the phthalocyanine system compound used as a component of an antireflection film are not restricted to an above-mentioned example, but even if they exfoliate in cresol the antireflection film which consists of a tetramethoxy phthalocyanine using the organic system resist ablation liquid made into a subject, they may exfoliate a dodeca fluoro phthalocyanine using inorganic system resist ablation liquid, such as a fuming nitric acid. Furthermore, although an example did not describe, when non-metal a non-replaced phthalocyanine is used, ashing can be performed and this can be removed.

[0052] In addition, the composition of a base, vacuum deposition conditions, development conditions, the kind of dry etching system, the kind of etching gas, etc. can be changed suitably.

[0053]

[Effect of the Invention] If this invention is applied so that clearly also from the above explanation, it will become possible to perform Fort Lee SOGUF1 with high resolution using the conformal antireflection film which consists of an organic compound. And it also becomes possible to design the antireflection film which has various optical properties using the versatility of a non-metal phthalocyanine system compound, and the selection width of face of a process is expanded.

[0054] this invention contributes to a raise in high integration of a semiconductor device, highly-efficient-izing, and reliance, and high yield-ization greatly through high-resolution-izing of a photolithography.

[Translation done.]